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**Water Rock Interaction [WRI 14]****Retention of aqueous  $^{226}\text{Ra}$  fluxes from a subaqueous mill tailings disposal at the Bois Noirs site (Loire, France)****Christelle Courbet<sup>a,\*</sup>, Caroline Simonucci<sup>a</sup>, Alexandre Dauzères<sup>a</sup>, Sylvain Bassot<sup>b</sup>, Arnaud Mangeret<sup>c</sup>, Jean-Michel Matray<sup>a</sup>**<sup>a</sup>*French Institute for Radiation protection and Nuclear Safety (IRSN), Radiation Protection Division (PRP), Nuclear Waste and Geosphere Department (DGE), SRTG/LETIS, B.P. 17, 92262 Fontenay-Aux-Roses, France*<sup>b</sup>*French Institute for Radiation protection and Nuclear Safety (IRSN), Radiation Protection Division (PRP), Nuclear Waste and Geosphere Department (DGE), SRTG/LAME, B.P. 17, 92262 Fontenay-Aux-Roses, France*<sup>c</sup>*French Institute for Radiation protection and Nuclear Safety (IRSN), Radiation Protection Division (PRP), Nuclear Waste and Geosphere Department (DGE), SEDRAN/BRN, B.P. 17, 92262 Fontenay-Aux-Roses, France*

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**Abstract**

This study focuses on a subaqueous mill tailings disposal site located in France (Bois Noirs) where 1.3 million tons of uranium mill sludge (fine tailings fraction < 50  $\mu\text{m}$ ) have been disposed since the 60's in a man-made pond below 4 meters of water maintained artificially by a rock-fill dam. A significant attenuation of aqueous  $^{226}\text{Ra}$  activity is observed in ground waters. This paper presents the preliminary modeling work performed for evaluating the role of water-rock interactions on aqueous  $^{226}\text{Ra}$  attenuation through the dam. This modeling attempt, assuming thermodynamic equilibrium, aims at checking the hydrochemical conceptual model developed in a previous study, in which Ra retention through the dam was assumed to most likely result from sorption onto metallic oxide-hydroxides. A 2D coupled reactive transport model was conceived to test this hypothesis over time and identify the measurements required to verify its consistency over the long term.

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*Keywords:* radium; mill tailings; natural attenuation; water cover; dam; retention; modeling.

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## 1. Introduction

Ensuring long-term performance of uranium mill tailings disposals is a significant concern for the next thousand years. This issue is mainly raised by the fate of long-lived uranium decay products such as thorium-230 (half-life of 80,000 yr) and radium-226 (1,600 yr) that were not removed by ore processing and are still present at their original activities in the resulting tailings [1]. These radionuclides continuously decay in the mill tailings piles, notably producing radon-222, a radioactive and carcinogenic gas that is known to induce lung cancer. Therefore, despite their short half-life (3.8 d), radon-222 emanations can still represent a long-term hazard around uranium mill tailings disposals because of their continuous production from long-lived parent decay. Among the different disposal options to cope with radiological emissions from mill tailings piles, a water cover is typically one of the most cost-efficient protections to (i) prevent acid production from tailings oxidation and (ii) reduce atmospheric emissions [2]. However, in the long run, this method generally depends on water management facilities and engineered structures such as dams to maintain water levels. It is quite unlikely that these structures will subsist for the thousands of years during which tailings will remain harmful. In this context, a safe and relatively maintenance-free disposal condition that might eliminate long-term concerns of acid generation and radiological hazards is required. With this objective in mind, understanding radionuclide attenuation processes is essential to evaluating long-term performance of uranium mill tailings disposal conditions.

In order to improve the knowledge about aqueous  $^{226}\text{Ra}$  attenuation processes, this study focuses on a subaqueous mill tailings disposal where 1.3 million metric tons of uranium mill sludge (fine tailings fraction  $< 50\ \mu\text{m}$ ) have been disposed since the 60's in a man-made pond below 4 meters of water maintained artificially by a rock-fill dam. A significant attenuation of aqueous  $^{226}\text{Ra}$  activity is observed in ground waters through the dam (Fig. 1), and this phenomenon was first studied by Combes and Schmitt [3]. This paper aims at presenting preliminary modeling work performed to evaluate the role of water-rock interactions on aqueous  $^{226}\text{Ra}$  attenuation through the dam, in order to assess its efficiency on the long term.

## 2. Hydrochemical Conceptual Model

A preliminary modeling attempt, assuming the thermodynamic equilibrium, has been performed with the CHESS code [4] in order to:

- identify the mineral association potentially controlling the pond water chemistry,
- identify the possible geochemical reactions occurring through the dam built of crushed granite, and which could explain the natural attenuation of aqueous  $^{226}\text{Ra}$ ,
- check the consistency with the first approach developed by Combes and Schmitt in 2006 [3] based on data measured by AREVA NC from 1996 to 2006.

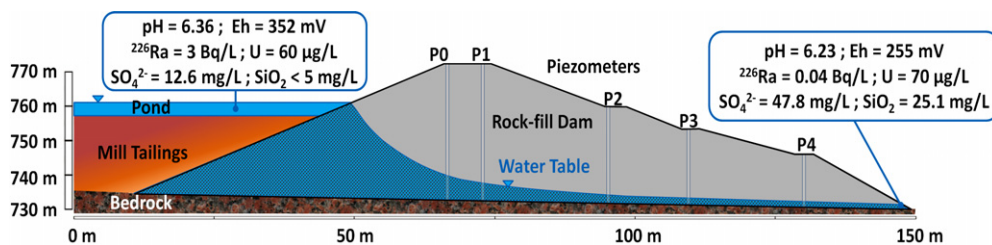


Fig. 1. Cross section through the dam and water chemistry along the flow path (measurements of October 2006) according to Combes and Schmitt [3].

Results of this first modeling step are consistent with the previous work [3], which concluded that the pond waters are roughly close to equilibrium with a paragenesis composed of ferric oxide-hydroxides, nontronite (iron(III)-rich member of the smectite group), soddyite ( $[\text{UO}_2]_2\text{SiO}_4 \cdot 2\text{H}_2\text{O}$ ), and barite ( $\text{BaSO}_4$ ). Barite seems to be the most likely source of sulfates in the tailings impoundment as no other sulfate mineral phase (such as gypsum or sulfurs) can explain the observed stoichiometry of the seasonal chemical fluctuations in the pond due to acidic rainwater recharge in autumn and winter (Fig. 2). These surface waters are however not at equilibrium with the atmospheric partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$ ) despite their high dissolved  $\text{O}_2$  content. Their moderately positive redox potential (only 350 mV) tends to indicate a complex atmosphere/water interaction leading to the oxygenation of waters (close to saturation) at the same time as maintaining the aqueous  $p\text{CO}_2$  at a higher level than in the atmosphere. This apparent thermodynamic disequilibrium seems to be an outcome of kinetic-controlled redox reactions (e.g. aerobic respiration) that could be further investigated in the future.

Titrated with an excess of pyrite, the simulated pond waters become more acidic and enriched in  $\text{SO}_4^{2-}$ , which could favor barite precipitation and thus trapping of  $^{226}\text{Ra}$  in the precipitated crystalline structure. However, this should lead to a drastic increase of dissolved  $\text{Fe(II)}$  concentration and to a concomitant reduction of Eh (as  $\text{O}_2$  is consumed by sulfur oxidation) according to CHES results. Such mechanisms are not observed across the dam where the decrease of pH (from 6.4 to 6.2) and Eh (from 350 to 250 mV) remains limited. Some lines of evidence (increasing  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  and  $\text{SiO}_2\text{aq.}$  concentrations), identified by [3], tend besides to indicate the hydrolysis of a silicate phase (e.g. plagioclase), which can only occur under acidic conditions ( $\text{pH} < 6$ ) in almost stagnant waters (to ensure a sufficient residence time since silicate hydrolysis is kinetically-controlled). As these conditions are not met in the drainage water across the dam, Combes and Schmitt [3] assumed that this reaction occurs in the vadose zone of the embankment when rainwaters slowly infiltrate and leach the sterile rock and/or during water table fluctuations in response to pond level rise and fall. This geochemical recharge can only lead to a slight decrease of pH and Eh through the dam and to a limited increase of metal and sulfate concentrations by sulfur oxidation, as only a small water volume within a much larger volume of rock is implied (compared with the saturated zone where all the sulfurs might have already been oxidized since the dam watering in the 60's). Moreover, according to CHES modeling, this concentrated vadose water input can lead to metallic oxide-hydroxide precipitation (hematite, goethite, etc.) in the saturated zone. Metallic oxide-hydroxides precipitation being well known to favor radium sorption [5] [6], this could thus explain Ra attenuation through the dam [3].

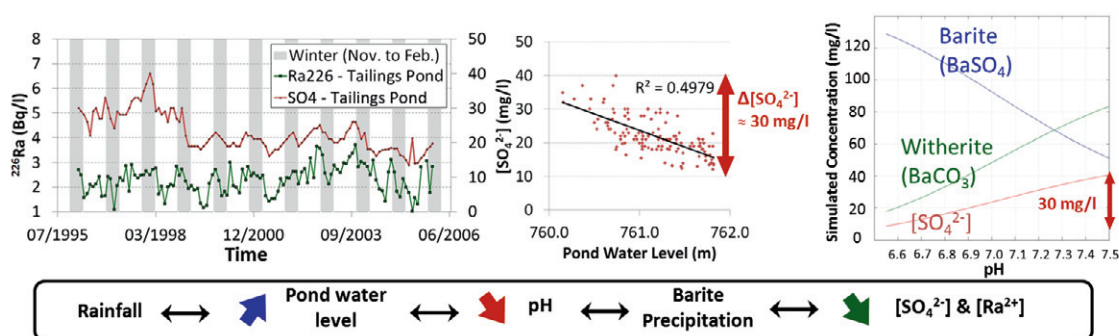


Fig. 2. Hydrochemical conceptual model of the pond water chemistry (from left to right : (a) Measured  $^{226}\text{Ra}$  and  $\text{SO}_4^{2-}$  concentrations from 01/1996 to 12/2005, (b) Measured  $\text{SO}_4^{2-}$  concentration vs. observed water level in the tailings pond, (c) Sulfate concentration increase simulated with CHES by barite dissolution and witherite precipitation over an increase of 1 pH unit).

### 3. Reactive Transport Modeling and Perspectives

In a second modeling step, these preliminary conclusions are tested in a coupled hydraulic and geochemical model built with the HYTEC code [7], considering a 2D cross section through the dam (Fig. 2). Observed water levels in the impoundment are used to build an upward-gradient fixed-head boundary condition, which varies over time on a monthly time-stepping basis. The downward-gradient condition is considered as a fixed potential given by the elevation of the water level downstream from the dam. The bedrock is assumed to be impervious (in comparison with the dam materials). Two water-level calibration strategies are tested in order to reproduce the water table profile across the dam over time:

- First, the tailings are assumed to be fully impervious; only the hydraulic parameters of the dam materials are calibrated and assumed to be uniform over space and time;
- Second, two homogenous hydraulic property zones are calibrated (one corresponding to the tailings and the other to the rock-fill embankment).

This modeling allows estimating the water flow per linear meter of dam, which can be compared with the drainage flow measured in the drains (which tends to decrease over time). These flow estimates can thus be used to assess the fluxes of  $^{226}\text{Ra}$  naturally retained in the dam, as well as  $\text{SO}_4^{2-}$ ,  $\text{SiO}_2$  and metals dissolved through the dam. This mass balance will be used to test the conceptual geochemical model deduced from CHESS by Combes and Schmitt [3], and to identify the measurements required to assess the long-term efficiency of  $^{226}\text{Ra}$  attenuation on this site. Particular emphasis will be given in the future to characterizing radium-bearing phases and hydraulic properties in the periodically rewetted zone of the dam through which the water table fluctuates.

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